

Appendix J

Planar Poly(*p*-phenylene) Derivatives. Ladder Formation for Maximization of Extended π -Conjugation

James M. Tour* and Jaydeep J. S. Lamba
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

Poly(*p*-phenylene) (PPP),¹ a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist^{1c,2} between the consecutive aryl units due to ortho hydrogen interactions (Fig 1). Attempts to enhance the solubility by

Figure 1

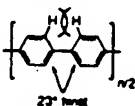
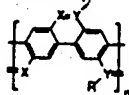


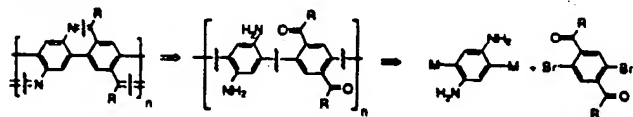
Figure 2



substitution of the rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).^{1i-k} Here we describe a synthetic route to ladder³ PPP derivatives with bridges that (1) form in high yields upon protonic activation once the PPP backbone is intact, (2) can be substituted so that the newly formed polymer is soluble, unlike many other aromatic ladder polymers, (3) contain a double-bonded unit to keep the consecutive aryl units planar while maximizing extended π -conjugation through the PPP backbone thereby increasing the band width (lowering the band gap) between the hydroquinoidal and quinoidal forms (Fig 2),^{1c} and (4) can be film cast in the uncyclized form followed by protonic activation to obtain films of the planarized system.

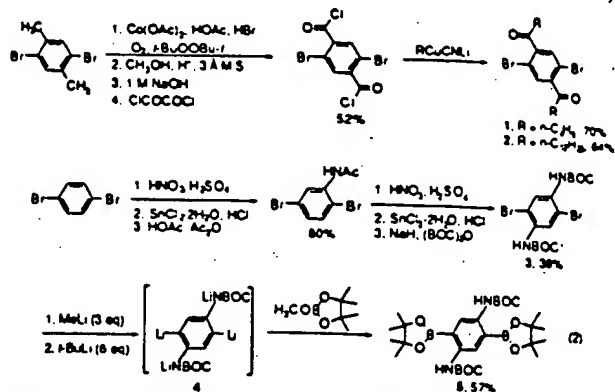
Our retrosynthetic approach involved two key steps (Scheme 1, M = metal). First, imine cleavage to the

Scheme 1



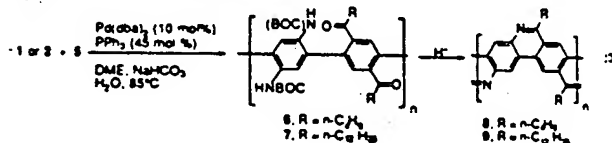
ketoamine functionalized PPP, and second, bond cleavage to the two arene systems shown. Since Pd(0)-catalyzed oxidative addition reactions are facilitated with electron deficient ring systems,⁴ we chose to keep the halides on the ketoaromatic portion.

After several nearly quantitative model reactions, we synthesized the two key monomers needed for the desired AB-type step growth polymerization (eqs 1 and 2).⁵ It is remarkable that while 3 was nearly insoluble in ether, it could be tetralithiated in ether to form a soluble intermediate 4 in almost quantitative yield (checked by addition of TMSCl and isolation of the arylbis(silane) after aqueous work-up). Treatment of 4 with methyl pinacol borate afforded the monomer 5 which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase (silica gel or neutral alumina caused rapid



decomposition of the intermediate) and CH_2Cl_2 as the eluant followed by recrystallized to form pure 5,6

Reaction of 1 or 2 with 5, in the presence of a Pd(0) catalyst, yielded the soluble polymers 6 and 7, respectively, from which size exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (6: 63% yield after fractional precipitation, $M_n = 9,850$ with $M_w/M_n = 1.85$; 7: 97% yield after fractional precipitation, $M_n = 28,400$ with $M_w/M_n = 3.70$). Upon exposure of 6 or 7 to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded 8 (90% yield) and 9 (97% yield), respectively (eq 3).^{7,8} All stretches for the ketone, carbamate, and amine in 6 and 7 were absent in the FTIR spectrum of 8 and 9.



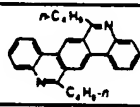
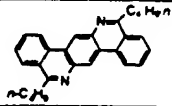
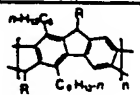
Samples of 8 and 9 can be solubilized with $\text{CH}_2\text{Cl}_2/\text{TFA}$ (3:2) mixtures. Additionally, 7 can form THF solution-cast films then be cleanly cyclized by suspension of the film in anhydrous HCl/EtOAc followed by proton removal with $\text{Et}_3\text{N}/\text{NaOH}$ to afford 9 as a flexible free-standing film. Again, this film was devoid of ketone, carbamate, and amine absorptions in the FTIR spectrum. Therefore, the dodecyl groups are apparently exerting a plasticizing effect so that even this planar rigid rod polymer can possess good film forming properties.

Powder X-ray diffraction (XRD) of annealed 8 showed a broad pattern at 14 and 41 Å while 9 showed a similar pattern at 27 and 45 Å. Differential scanning calorimetry (DSC) (50–350°C, 20°C/min, N_2) thermograms of 8 and 9 were featureless on both the first and second heating cycles. Thermogravimetric analysis (TGA) (50–900°C, 20°C/min, N_2) of 9 showed an onset of major weight loss at 400°C, 10% weight loss at 434°C, and 50% weight loss at 550°C. The TGA thermogram of 8 was similar.

Most exciting is the optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of 6 to 8 and 7 to 9): an observation consistent with the proposed ladder formation (Table I). Also interesting are the large hypsochromic

shift in the spectrum of protonated 9 (solution) relative to 9 in the neutral form (solid), suggesting that cationic nitrogen atoms retard the extended conjugation. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers, 9 oligo(*p*-phenylenes), and PPP,¹⁰ while the λ_{\max} values are in the range of other near-planar PPP derivatives that have been synthesized.¹²

Table I. Optical Absorption Data

Compound	λ in solution (nm) ^a	λ of solid (nm) ^a
6	CH ₂ Cl ₂ : 250, 306 (sh)	248, 308 ^b
7	CH ₂ Cl ₂ : 250, 388	250, 398 ^b
8	CH ₂ Cl ₂ /TFA: 374, <u>396</u> , 426 (sh), 514, 520 (ed) ^c	-----
9	CH ₂ Cl ₂ /TFA: 376, <u>400</u> , 428, 478, 516, 530 (ed) ^c	463-490 ^d
	CH ₂ Cl ₂ : 300 (ref 9)	-----
	CH ₂ Cl ₂ : 294 (ref 9)	-----
<i>p</i> -sexiphenylene	CHCl ₃ : <u>318</u> (ref 10)	-----
PPP (calcd infinite <i>M_n</i>)	344 (ref 10)	-----
	CH ₂ Cl ₂ : <u>348-443</u> (ref 12)	-----

^a λ_{\max} is underlined. (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{\max} intensity. ^bAlso a strong carbonyl absorption at 196 nm. ^cSpectrum recorded on the acid solubilized, therefore, multiprotonated system. ^dThese λ_{\max} values were recorded on a series of four different polymer samples of 9 in order to insure their reproducibility.¹¹

Acknowledgments. We are grateful for support from the Office of Naval Research, the Defense Advanced Research Projects Agency, the National Science Foundation (EHR-91-08772, DMR-9158315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96): Hercules, IBM, Ethyl, Shell, and Eli Lilly Corporations. We also thank Molecular Design Ltd. for the use of their synthetic data base.

References and Notes

- (1) For some recent reviews on polyphenylene, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* 1987, 87, 357. (b) Noren, G. K.; Stille, J. K. *Macromol. Rev.* 1971, 5, 385. (c) Elsenbaumer, R. L.; Shacklette, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (d) Tourillon, G. in ref 1c. (e) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* 1982, 82, 209. For some *p*-phenylene decamer to be 22.3° using MMX with extended π -Hückel parameters. For a discussion of twist angle versus degree of extended conjugation, see: (a) Brédas, J. L. in ref 1c. (b) Ferraris, J. P.; Andrus, R. G.; Hrnčir, D. C. *J. Chem. Soc., Chem. Commun.* 1989, 1318. (c) Gorman, C. B.; Ginsburg, E. J.; Moore, J. S.; Grubbs, R. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, 32(3), 714. (d) Orchard, B. J.; Freidenreich, B.; Tripathy, S. K. *Polymer* 1986, 27, 1533.
- (3) For some discussions of aromatic ladder polymers, see: (a) Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* 1970, 7, 113. (b) Schlüter, A.-D. *Adv. Mater.* 1991, 3, 282. (c) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* 1990, 2, 649. (d) Hong, S. Y.; Kertesz, M.; Lee, Y. S.; Kim, O.-K. *Chem. Mater.* 1992, 4, 378. (e) Godt, A.; Schlüter, A.-D. *Adv. Mater.* 1991, 3, 497. (f) Yu, L.; Dalton, L. R. *Macromolecules* 1990, 23, 3439.
- (4) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* 1981, 11, 513. (b) Siddiqui, M. A.; Snieckus, V. *Tetrahedron Lett.* 1988, 29, 5463. (c) Gronowitz, S.; Lawitz, K. *Chem. Scripta* 1984, 24, 5.
- (5) (a) The *tert*-butylperoxide modified Co-based oxidation was far superior to several permanganate oxidations attempted. See: Hay, A. S.; Blanchard, H. S. *Canad. J. Chem.* 1965, 43, 1306. The dicarboxylic acid was then converted to the diester to facilitate purification. (b) Doornbos, T.; Strating, J. *Org. Prep. Proced.* 1969, 1, 287.
- (6) The arylbis(boronic acid) analog of 5 could not be adequately purified for the step growth polymerization.
- (7) The twist in 8 and 9 is <1° between the consecutive phenyl rings calculated by MMX with extended π -Hückel parameters.
- (8) Highest molecular weight samples of 6 and 7 were obtained when the Pd-catalyzed coupling was done for ~24 h using an equimolar mixture of 1:5 or 2:5, respectively, followed by the addition of a 5-10 mol % excess of 5 with continued heating for 1-2 d. 6: Anal. calc'd for (C₃₂H₄₂N₂O₆)_n: C, 69.79; H, 7.69; N, 5.07. Found: C, 70.55; H, 7.25; Br, <0.5; N, 5.13. 7: Anal. calc'd for (C₄₈H₇₄N₂O₆)_n: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.99; H, 9.40; Br, <0.5; N, 3.55. 8: Anal. calc'd for (C₂₂H₂₂N₂)_n: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56. 9: Anal. calc'd for (C₃₈H₅₄N₂)_n: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.
- (9) The planar trimers were prepared during our model studies for the polymerizations described here using Pd-catalyzed couplings.
- (10) Ried, W.; Freitag, D. *Angew. Chem. Intern. Ed. Engl.* 1968, 7, 835.
- (11) Drs. R. Gaudiana and P. Mehta of Polaroid Corporation kindly provided the solid-state UV-vis data.
- (12) The near-planar benzenoid ladder polymers were prepared by Pd-catalyzed couplings. See: Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* 1991, 12, 489. Scherf, U.; Müllen, K. *Synthesis* 1992, 23. Scherf, U.; Müllen, K. *Macromolecules* 1992, 25, 3546.